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45152 (US). **SHIH, Keith, S.** [US/US]; 10154 Elmfield Drive, Loveland, OH 45140 (US).

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(74) Agents: **STEWART, Richard, C.** et al.; International Paper Company, 6285 Tri-Ridge Boulevard, Loveland, OH 45140 (US).

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(71) Applicant (*for all designated States except US*): **INTERNATIONAL PAPER COMPANY** [US/US]; 6400 Poplar Avenue, Memphis, TN 38197 (US).

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(72) Inventors; and

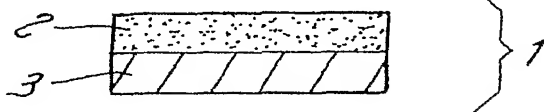
(75) Inventors/Applicants (*for US only*): **RUDOLPH, Richard, F.** [US/US]; 5095 Greentrail Lane, Mason, OH 45040 (US). **HONG, Yaoliang** [CN/US]; 6754 Man O War Lane, Mason, OH 45040 (US). **MILLER, Derek, L.** [US/US]; 4409 W Harold Avenue, Visalia, CA 93291 (US). **HUANG, Yan, C.** [US/US]; 4341 McKeever Pike, Williamsburg, OH 45176 (US). **YANG, Sen** [US/US]; 8377 Ashmont Way, Mason, OH 45040 (US). **SONG, Jay, C.** [US/US]; 7 Yale Drive, Highland Mills, NY 10930 (US). **LIGUZINSKI, Benjamin, Thomas** [US/US]; 5735 Sidney Road, Cincinnati, OH 45233 (US). **BUCHER, Ewa, Gertruda** [US/US]; 520 Quail Court, Lebanon, OH 45036 (US). **TAN, Zheng** [CA/US]; 5261 Balsam Place Apt. 205, Mason, OH 45040 (US). **KULKARNI, Sandeep** [US/US]; 6074 Wedgewood Drive, Morrow, OH

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(54) Title: A PAPER SUBSTRATE CONTAINING A FUNCTIONAL LAYER AND METHODS OF MAKING AND USING THE SAME



(57) Abstract: The invention relates to the papermaking art and, in particular, to the manufacture of paper or paperboard substrates, paper-containing articles such as multilayered paper or paperboard or corrugated-based packaging having a functional layer, as well as methods of making and using the same.

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A PAPER SUBSTRATE CONTAINING A FUNCTIONAL LAYER AND METHODS OF  
MAKING AND USING THE SAME

Cross Reference of Prior Applications

The present invention is related to, and claims the benefit of 119(e) priority to U.S. provisional patent application Ser. No. 60/698,274; entitled "MULTILAYERED PAPER OR PAPERBOARD SUBSTRATE HAVING IMPROVED SULFUR DIOXIDE HOLDOUT", which was filed on July 11, 2005, and is hereby incorporated, in its entirety, herein by reference. This application is also related to and claims the benefit of 119(e) priority to U.S. provisional patent application Ser. No. 60/734,021; entitled "PAPER SUBSTRATE CONTAINING A FUNCTIONAL LAYER, AS WELL AS METHODS OF MAKING AND USING THE SAME", which was filed on November 4, 2005, and is hereby incorporated, in its entirety, herein by reference.

Field of the Invention

The invention relates to the papermaking art and, in particular, to the manufacture of paper or paperboard substrates, paper-containing articles such as multilayered paper or paperboard or corrugated-based packaging, having a functional layer, as well as methods of making and using the same.

Background of the Invention

Paper substrates containing functional layers are highly desired by several niche markets. Each functional layer may be specifically tailored to each market demand and specifications depending on the packaging requirement for consumer goods. These packaging requirements are

specifically determined by the risks associated with packaging and shipping such goods around the country and around the world. However, such demands from such markets may require functionalities to be programmed within the functional layer of paper substrate that, when the paper substrate is incorporated into a package, the functionality itself prohibit and/or make it costly and/or less efficient to manufacture and/or convert the substrate so as to be incorporated into a paper-based package. Accordingly, there is an unmet need for all markets to be able to program tailored functionality into a coating layer of a paper substrate (e.g. based upon the nature of the consumer goods to be packaged and/or shipped) so that, when the paper substrate is incorporated into a such packages, there is little or no loss of manufacturing/conversion efficiency and thus little or no increase in overhead costs for production of such packages.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1: A first schematic cross section of just one exemplified embodiment of the paper substrate that is included in the paper substrate of the present invention.

Figure 2: A second schematic cross section of just one exemplified embodiment of the paper substrate that is included in the paper substrate of the present invention.

Figure 3: A third schematic cross section of just one exemplified embodiment of the paper substrate that is included in the paper substrate of the present invention.

Figure 4: A exemplified embodiment of a package blank that contains the substrate of the present invention.

Figure 5: A close-up view of a flap portion of the package blank shown in Figure 4 wherein a treated portion is shown as covering at least a part of the flap.

Figure 6: A section view of an untreated portion of the flap portion in Figure 5 shown taken along section line 6-6 of Figure 5.

Figure 7: A section view of a treated portion of the flap portion in Figure 5 shown taken along section line 7-7 of Figure 5.

#### DETAILED DESCRIPTION OF THE INVENTION

The inventors have surprisingly found a paper substrate containing a functional layer that, when incorporated into a package for shipping, is capable of minimizing the costly impact of that functionality on the downstream manufacturing/converting requirements by increasing manufacturing/converting efficiency that otherwise would render the use of such functionality cost prohibitive.

The paper substrate contains a web of cellulose fibers. The source of the fibers may be from any fibrous plant. In certain embodiments, at least a portion of the pulp fibers may be provided from non-woody herbaceous plants including, but not limited to, kenaf, hemp, jute, flax, sisal, or abaca although legal restrictions and other considerations may make the utilization of hemp and other fiber sources impractical or impossible. The paper substrate of the present invention may contain recycled fibers and/or virgin fibers. Recycled fibers differ from virgin

fibers in that the fibers may have gone through the drying process at least once, preferably several times.

The paper substrate of the present invention may contain from 1 to 99 wt%, preferably from 5 to 95 wt%, most preferably from 60 to 80 wt% of cellulose fibers based upon the total weight of the substrate, including 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 99 wt%, and including any and all ranges and subranges therein.

Preferably, the sources of the cellulose fibers are from softwood and/or hardwood. The paper substrate of the present invention may contain from 1 to 100 wt%, preferably from 5 to 95 wt%, cellulose fibers originating from softwood species based upon the total amount of cellulose fibers in the paper substrate. This range includes 1, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 100wt%, including any and all ranges and subranges therein, based upon the total amount of cellulose fibers in the paper substrate.

The paper substrate may alternatively or overlappingly contain from 0.01 to 100 wt% fibers from softwood species, preferably from 0.1 to 95wt%, most preferably from 1 to 90wt% based upon the total weight of the paper substrate. The paper substrate contains not more than 0.01, 0.05, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 100wt% fibers from softwood species based upon the total weight of the paper substrate, including any and all ranges and subranges therein.

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The paper substrate of the present invention may contain from 1 to 100 wt%, preferably from 5 to 95 wt%, cellulose fibers originating from hardwood species based upon the total amount of cellulose fibers in the paper substrate. This range includes 1, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 100wt%, including any and all ranges and subranges therein, based upon the total amount of cellulose fibers in the paper substrate.

The paper substrate may alternatively or overlappingly contain from 0.01 to 100 wt% fibers from hardwood species, preferably from 5 to 95 wt%, cellulose fibers originating from hardwood species based upon the total amount of cellulose fibers in the paper substrate. The paper substrate contains not more than 0.01, 0.05, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 99 and 100wt% fibers from hardwood species based upon the total weight of the paper substrate, including any and all ranges and subranges therein.

When the paper substrate contains both hardwood and softwood fibers, it is preferable that the hardwood/softwood ratio be from 0.001 to 1000. This range may include 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 200, 300, 400, 500, 600, 700, 800, 900, and 1000 including any and all ranges and subranges therein and well as any ranges and subranges therein the inverse of such ratios.

Further, the softwood and/or hardwood fibers contained by the paper substrate of the present invention may be modified by physical and/or chemical means. Examples of physical

means include, but is not limited to, electromagnetic and mechanical means. Means for electrical modification include, but are not limited to, means involving contacting the fibers with an electromagnetic energy source such as light and/or electrical current. Means for mechanical modification include, but are not limited to, means involving contacting an inanimate object with the fibers. Examples of such inanimate objects include those with sharp and/or dull edges. Such means also involve, for example, cutting, kneading, pounding, impaling, etc means.

Examples of chemical means include, but is not limited to, conventional chemical fiber modification means including crosslinking and precipitation of complexes thereon. Examples of such modification of fibers may be, but is not limited to, those found in the following patents 6,592,717, 6,592,712, 6,582,557, 6,579,415, 6,579,414, 6,506,282, 6,471,824, 6,361,651, 6,146,494, H1,704, 5,731,080, 5,698,688, 5,698,074, 5,667,637, 5,662,773, 5,531,728, 5,443,899, 5,360,420, 5,266,250, 5,209,953, 5,160,789, 5,049,235, 4,986,882, 4,496,427, 4,431,481, 4,174,417, 4,166,894, 4,075,136, and 4,022,965, which are hereby incorporated, in their entirety, herein by reference.

Sources of "Fines" may be found in SaveAll fibers, recirculated streams, reject streams, waste fiber streams. The amount of "fines" present in the paper substrate can be modified by tailoring the rate at which such streams are added to the paper making process.

The paper substate preferably contains a combination of hardwood fibers, softwood fibers and "fines" fibers. "Fines" fibers are, as discussed above, recirculated and are typically not more than 100  $\mu\text{m}$  in length on average, preferably not more than 90  $\mu\text{m}$ , more preferably not more than

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80  $\mu\text{m}$  in length, and most preferably not more than 75  $\mu\text{m}$  in length. The length of the fines are preferably not more than 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 100  $\mu\text{m}$  in length, including any and all ranges and subranges therein.

The paper substrate contains from 0.01 to 100 wt% fines, preferably from 0.01 to 50wt%, most preferably from 0.01 to 15wt% based upon the total weight of the substrate. The paper substrate contains not more than 0.01, 0.05, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 100wt% fines based upon the total weight of the paper, including any and all ranges and subranges therein.

The paper substrate may alternatively or overlappingly contain from 0.01 to 100 wt% fines, preferably from 0.01 to 50wt%, most preferably from 0.01 to 15wt% based upon the total weight of the fibers contained by the paper substrate. The paper substrate contains not more than 0.01, 0.05, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 100wt% fines based upon the total weight of the fibers contained by the paper substrate, including any and all ranges and subranges therein.

The paper substrate may also contain a functional layer.

The functional layer may contain additives that permit the layer to be a holdout layer. Examples of a holdout layer may be those that holdout or reduce the penetration of grease, water, water vapor, salt air, carbon dioxide, sulfur dioxide, hydrogen sulfide, or other solids/gases/liquids which pose a threat to surfaces of, for example, metallic objects,



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consumables such as fruits and vegetables, as well as other consumer/manufacturing goods. Examples of paper substrates containing holdout layers include United States Published Patent Applications 20020182381; 20040221976 and US provisional applications having USSNs 60/698,274 filed July 11, 2005 and 60/731,897, filed on October 31, 2005, which are hereby incorporated, in their entirety, herein by reference. The functional layer may contain the additives mentioned in these applications so as to impart such functionality in the layer, the substrate, and resulting package made therefrom.

The functional layer may also contain releasable additives. An example of a releasable additive may be vapor corrosion inhibitors. Examples of such inhibitors may be found in US patents 6,833,334; 6,617,415; 6,555,600; 6,444,595; 6,420,470; 6,331,044; 6,292,996; 6,156,929; 6,132,827; 6,054,512; 6,028,160; 5,937,618; 5,896,241; 5,889,639; 5,773,105; 5,736,231; 5,715,945; 5,712,008; 5,705,566; 5,486,308; 5,391,322; 5,324,448; 5,139,700; 5,209,869; 5,344,589; 4,313,836; 4,312,768; 4,151,099; 4,101,328; 6,429,240; 6,273,993; 6,255,375; and 4,685,563 and in US application having USSN 60/731,897, filed on October 31, 2005, which are all hereby incorporated, in their entirety, herein by reference.

The functional layer may also contain an antifouling agent and/or antimicrobial agent and may serve to be antifouling and/or antimicrobial. Alternatively, it may serve to release such antifouling and/or antimicrobial agents into the local environment. Examples of such antimicrobial agents are those found in United States Published Patent Applications 20020182381; 20040221976, and United States applications having USSNs 60/585757; 11/175899; and 11/175700, which are hereby incorporated, in their entirety, herein by reference.

In one specific embodiment, the paper substrate of the present invention may contain a functional layer containing a film-forming compound. Although the film-forming compound may be any film-forming compound, examples of preferred film-forming compounds may be those that have T<sub>g</sub>, glass transition temperatures, of not greater than 350°C. The T<sub>g</sub> may be any T<sub>g</sub>, but preferably not greater than 350, 340, 330, 325, 320, 310, 300, 290, 280, 275, 270, 260, 250, 225, 200, 175, 150, 125, and 100, including any and all ranges and subranges therein. An example of such a film forming compound is a styrene acrylate-containing compound such as Dow latex 229804 and/or starch such as Ethylex 2035 Starch. The film forming compound may be present in the functional layer from 0 to 100%, preferably from 50 to 150 ppm, based on the total weight of the functional layer, including 0, 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, and 95 wt% based on the total weight of the functional layer, including any and all ranges and subranges therein. In ppm, the film forming compound may be present in the functional layer at any amount, preferably 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, and 150 ppm based on the total weight of the functional layer, including any and all ranges and subranges therein.

The functional layer may be present at any weight. The functional layer may be present at a weight that ranges from 1 to 25 gsm, preferably from 2 to 20 gsm, more preferably from 3 to 18 gsm (grams per square meter), and most preferably from 5 to 15 gsm. This includes, but is not limited to, embodiments where the functional layer is added to the fibers at the size press and/or coater. The amount of functional layer include 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, and 25 gsm, including any and all ranges and subranges therein.

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Further, the functional layer may contain any crosslinker. A preferable crosslinker is one such as Cartabond TSI. Still further, the functional layer may contain a pigment which can act as an anti-blocking agent. Any clay or anti-blocking agent is acceptable. A preferable pigment is a clay. A preferable clay is one such as NuClay. Still further, the functional layer may contain a defoamer. The crosslinker may be present from 0.1 to 10 ppm based on the total weight of the functional layer, preferably 0.1, 0.2, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5, 3, 4, 5, 6, 7, 8, 9, and 10 ppm based on the total weight of the functional layer, including any and all ranges and subranges therein. The pigment may be present from 50 to 150 ppm based on the total weight of the functional layer, preferably 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, and 150 ppm based on the total weight of the functional layer, including any and all ranges and subranges therein. The defoamer may be present from 50 to 150 ppm, preferably 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, and 150 ppm based on the total weight of the functional layer, including any and all ranges and subranges therein.

The functional layer, when contacted with the fibers of the paper substrate, may have any pH, preferably from 4 to 8, including 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5 and 8, including any and all ranges and subranges therein. The functional layer, when contacted with the fibers, may have any % solids, preferably a % solids of from 1 to 65, more preferably from 10 to 60% solids, including 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60% solids, including any and all ranges and subranges therein. The functional layer, when contacted with the fibers, may have a Brookfield Viscosity @ 100 rpm of  $\leq 1000$  cps, preferably  $\leq 300$  cps, most preferably from 50 to 200 cps, including 50, 55, 60, 65, 70, 75, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, and 200 cps, including

any and all ranges and subranges therein.

Figures 1-3 demonstrate different embodiments of the paper substrate 1 in the paper substrate of the present invention. The invention is not limited thereto these examples. Figure 1 demonstrates a paper substrate 1 that has a web of cellulose fibers 3 and a functional layer 2 where the functional layer 2 has minimal or no interpenetration of the web of cellulose fibers 3. Such an embodiment may be made, for example, when a functional layer is coated onto a web of cellulose fibers. Addition points may be at the size press or coater as well, for example.

Figure 2 demonstrates a paper substrate 1 that has a web of cellulose fibers 3 and a functional layer 2 where the functional layer 2 interpenetrates the web of cellulose fibers 3. The interpenetration layer 4 of the paper substrate 1 defines a region in which at least functional layer 2 penetrates into and is among the cellulose fibers. The interpenetration layer may be from 1 to 99%, preferably less than 50%, more preferably less than 25% of the entire cross section of at least a portion of the surface of the paper substrate, including 1, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 99% of the paper substrate, including any and all ranges and subranges therein. Such an embodiment may be made, for example, when a functional layer is added to the cellulose fibers prior to a coating method and may be combined with a subsequent coating method if required. Addition points may be at the size press, for example.

Figure 3 demonstrates a paper substrate 1 that has a web of cellulose fibers 3 and a functional layer 2 where the functional layer 2 is approximately evenly distributed throughout the web of cellulose fibers 3. Such an embodiment may be made, for example, when a functional

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layer is added to the cellulose fibers prior to a coating method and may be combined with a subsequent coating method if required. Exemplified addition points may be at the wet end of the paper making process, the thin stock, and the thick stock.

The density, basis weight and caliper of the web of this invention may vary widely and conventional basis weights, densities and calipers may be employed depending on the paper-based product formed from the web. Paper or paperboard of invention preferably have a final caliper, after calendering of the paper, and any nipping or pressing such as may be associated with subsequent coating of from about 1 mils to about 35 mils, although the caliper can be outside of this range if desired. More preferably the caliper is from about 4 mils to about 20 mils, and most preferably from about 7 mils to about 17 mils. The caliper of the paper substrate with or without any functional layer may be 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 20, 22, 25, 27, 30, 32, and 35, including any and all ranges and subranges therein.

Paper substrates of the invention preferably exhibit basis weights of from about 10 lb/3000ft<sup>2</sup> to about 500 lb/3000ft<sup>2</sup>, although web basis weight can be outside of this range if desired. More preferably the basis weight is from about 30lb/3000ft<sup>2</sup> to about 200 lb/3000ft<sup>2</sup>, and most preferably from about 35 lb/3000ft<sup>2</sup> to about 150 lb/3000ft<sup>2</sup>. The basis weight may be 10, 12, 15, 17, 20, 22, 25, 30, 32, 35, 37, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 225, 250, 275, 300, 325, 350, 375, 400, 425, 450, 500 lb/3000ft<sup>2</sup>, including any and all ranges and subranges therein.

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The final density of the papers may be calculated by any of the above-mentioned basis weights divided by any of the above-mentioned calipers, including any and all ranges and subranges therein. Preferably, the final density of the papers, that is, the basis weight divided by the caliper, is preferably from about 6 lb/3000ft<sup>2</sup>/mil to about 14 lb/3000ft<sup>2</sup>/mil although web densities can be outside of this range if desired. More preferably the web density is from about 7 lb/3000ft<sup>2</sup>/mil to about 13 lb/3000ft<sup>2</sup>/mil and most preferably from about 9 lb/3000ft<sup>2</sup>/mil to about 12 lb/3000ft<sup>2</sup>/mil.

The substrate of the present invention preferably has a Cobb Value as determined by the Cobb Sizing Test, according to ASTM D-3285 (TAPPI T-441), of less than 50 g/m<sup>2</sup>, preferably less than 35 g/m<sup>2</sup>, more preferably less than 30 g/m<sup>2</sup>, most preferably less than 25 g/m<sup>2</sup>. The Cobb Value may be 50, 45, 40, 35, 34, 33, 32, 31, 30, 29, 28, 27, 26, 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1 g/m<sup>2</sup>, or less, including any and all ranges and subranges therein.

Textbooks such as those described in the "Handbook for pulp and paper technologists" by G.A. Smook (1992), Angus Wilde Publications, which is hereby incorporated, in its entirety, by reference. Further, G.A. Smook referenced above and references cited therein provide lists of conventional additives that may be contained in the paper substrate, and therefore, the paper articles of the present invention. Such additives may be incorporated into the paper, and therefore, the paper packaging (and packaging materials) of the present invention in any conventional paper making process according to G.A. Smook referenced above and references cited therein.

The paper substrate of the present invention may also include optional substances including retention aids, sizing agents, binders, fillers, thickeners, and preservatives. Examples of fillers include, but are not limited to; clay, calcium carbonate, calcium sulfate hemihydrate, and calcium sulfate dehydrate. Examples of binders include, but are not limited to, polyvinyl alcohol, polyamide-epichlorohydrin, polychloride emulsion, modified starch such as hydroxyethyl starch, starch, polyacrylamide, modified polyacrylamide, polyol, polyol carbonyl adduct, ethanediol/polyol condensate, polyamide, epichlorohydrin, glyoxal, glyoxal urea, ethanediol, aliphatic polyisocyanate, isocyanate, 1,6 hexamethylene diisocyanate, diisocyanate, polyisocyanate, polyester, polyester resin, polyacrylate, polyacrylate resin, acrylate, carboxymethyl cellulose, urea, sodium nitrate, and methacrylate. Other optional substances include, but are not limited to silicas such as colloids and/or sols. Examples of silicas include, but are not limited to, sodium silicate and/or borosilicates. Another example of optional substances is solvents including but not limited to water.

Further, the starch may be of any type, including but not limited to oxidized, ethylated, cationic and pearl, and is preferably used in aqueous solution. Illustrative of useful starches for the practice of this preferred embodiment of the invention are naturally occurring carbohydrates synthesized in corn, tapioca, potato and other plants by polymerization of dextrose units. All such starches and modified forms thereof such as starch acetates, starch esters, starch ethers, starch phosphates, starch xanthates, anionic starches, cationic starches and the like which can be derived by reacting the starch with a suitable chemical or enzymatic reagent can be used in the practice of this invention.

Useful starches may be prepared by known techniques or obtained from commercial sources. Suitable starches include, but are not limited to, PG-280 from Penford Products, SLS-280 from St. Lawrence Starch, the cationic starch CatoSize 270 from National Starch and the hydroxypropyl No. 02382 from Poly Sciences, Inc.

Starches for use in the practice of this invention may be modified starches. Still further, are those starches that are cationic modified or non-ionic starches such as CatoSize 270 and KoFilm 280 (all from National Starch) and/or chemically modified starches such as PG-280 ethylated starches and AP Pearl starches. Starches for use in the practice of this invention may be cationic starches and chemically modified starches.

The contacting of the functional layer with the cellulose fibers may occur anytime in the papermaking process including, but not limited to the wet end, thick stock, thin stock, head box, size press and coater, with the preferred addition point being at the size press and/or coater. Further addition points include machine chest, stuff box, and suction of the fan pump. As discussed above and in Figure 3, when the functional layer components are added towards the wet end of papermaking, the functional layer may become interpenetrated and/or incorporated into the paper substrate layer containing fibers.

The paper substrate may be made by contacting further optional substances with the cellulose fibers as well. The contacting may occur anytime in the papermaking process including, but not limited to the thick stock, thin stock, head box, size press, water box, and coater. Further



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addition points include machine chest, stuff box, and suction of the fan pump. The cellulose fibers, functional layer, and/or optional/additional components may be contacted serially, consecutively, and/or simultaneously in any combination with each other. The cellulose fibers and functional layer may be pre-mixed in any combination before addition to or during the paper-making process.

The paper substrate may be pressed in a press section containing one or more nips. However, any pressing means commonly known in the art of papermaking may be utilized. The nips may be, but is not limited to, single felted, double felted, roll, and extended nip in the presses. However, any nip commonly known in the art of papermaking may be utilized.

The paper substrate may be dried in a drying section. Any drying means commonly known in the art of papermaking may be utilized. The drying section may include and contain a drying can, cylinder drying, Condebelt drying, IR, or other drying means and mechanisms known in the art. The paper substrate may be dried so as to contain any selected amount of water. Preferably, the substrate is dried to contain less than or equal to 10% water.

The paper substrate may be passed through a size press, where any sizing means commonly known in the art of papermaking is acceptable. The size press, for example, may be a puddle mode size press (e.g. inclined, vertical, horizontal) or metered size press (e.g. blade metered, rod metered). At the size press, sizing agents such as binders may be contacted with the substrate. Optionally these same sizing agents may be added at the wet end of the papermaking process as needed. After sizing, the paper substrate may or may not be dried again according to

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the above-mentioned exemplified means and other commonly known drying means in the art of papermaking. The paper substrate may be dried so as to contain any selected amount of water. Preferably, the substrate is dried to contain less than or equal to 10% water.

In addition to the starch and/or polyvinyl alcohol being added at the size press/coater section(s), small amounts of other additives may be present as well in the size composition. These include, without limitation, dispersants, fluorescent dyes, surfactants, deforming agents, preservatives, pigments, binders, pH control agents, coating releasing agents, optical brighteners, defoamers, bulking agents such as expandable microspheres and the like. Such additives may include any and all of the above-mentioned optional substances, or combinations thereof.

The paper substrate may be calendered by any commonly known calendaring means in the art of papermaking. More specifically, one could utilize, for example, wet stack calendaring, dry stack calendaring, steel nip calendaring, hot soft calendaring or extended nip calendaring, etc.

The paper substrate may contain multiple layers of cellulose fibers webs. Preferably, the substrate contains at least three layers of cellulose fiber webs having six major surfaces or four layers of cellulose fiber webs having eight major surfaces. Any of these surfaces may be corrugated, laminated, glued, or adhered to each other in any conventional manner so as to form a multilayered substrate. Preferably, a multilayered paper substrate may be a corrugated paper substrate. In one embodiment of the invention, a corrugated paper substrate may be made from the paper substrate of the present invention and further converted/folded/die cut into for example a package and/or shipping material that is, single layered and/or multilayered paper or paperboard

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material. The package and/or shipping material preferably comprises at least three paper substrates, each having a web of cellulose fibers and at least one of which further containing the functional layer therein and/or thereon.

These above-mentioned methods of making the paper substrate of the present invention may be added to any conventional papermaking processes, as well as converting processes, including corrugating, abrading, sanding, slitting, scoring, perforating, sparking, calendaring, sheet finishing, converting, coating, laminating, printing, etc. Preferred conventional processes include those tailored to produce paper substrates capable to be utilized as coated and/or uncoated paper products, board, and/or substrates. Textbooks such as those described in the "Handbook for pulp and paper technologists" by G.A. Smook (1992), Angus Wilde Publications, which is hereby incorporated, in its entirety, by reference.

Within the above-mentioned conventional papermaking processes, as well as converting processes, multilayered paper-based structures (e.g. such as those mentioned above) are formed and/or folded into shapes useful for packaging and/or shipping. During this time, means for connecting such layers together are required. Such means may be gluing, laminating, adhering and/of folding such layers together and require, in part, an adhesive.

Accordingly, the paper substrate and articles made therefrom preferably contain an adhesive layer.

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Figure 6 shows one embodiment of the paper substrate of the present invention which may contain a web of cellulose fibers 3 and a functional layer 2 and an adhesive layer 5. Of course, the above-mentioned Figures 1-3 pertain to when the functional layer is present. Such embodiments may also be appropriately suited for when an adhesive layer is utilized in addition thereto. In fact, there may be a multi-layered structure within each paper substrate (e.g. fiber web, functional layer, and/or adhesive) and these layers may be applied in any order and/or fashion. Further, the web, functional layer, and adhesive layer may be one layer and/or may interpenetrate one another within an interpenetration layer 4 from 0 to 100%, respectively, and/or each independent of the other to any degree. The state of interpenetration for any two or more of the web, functional layer and adhesive layer may be 1, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 99% of the paper substrate, including any and all ranges and subranges therein.

The adhesive layer preferably contains at least one adhesive that is suitable for adhering two layers of cellulose fiber web together. Any conventional adhesive is suitable. Examples of suitable adhesives include those known as hot melt adhesives and/or cold-set adhesives. Examples of the adhesive are those containing a polyamide, polyamide containing polymer, polyamide containing copolymer, polyethylene, polyethylene-containing polymer, polyethylene-containing copolymer, ethylene vinyl acetate, ethylene vinyl acetate-containing polymer, ethylene vinyl acetate copolymer, vinyl, polyvinyl, vinyl containing polymer, vinyl containing copolymer, poly, alpha olefin, olefin, polyolefin, olefin containing polymer, and olefin containing copolymer. Commercial hot melt adhesives include those from National Starch, Hercules, Henkel, Reynolds, Arizona Chemical Company, and HB Fuller. Specific examples are Henkel 80-8795; Chief 235

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HP; National Starch 34-246A; Chief 235 Plus; HB Fuller HL9254; Henkel TB9-15-5; National Starch 34-6601; National Starch 34-379A; Forbo/Swifts; Pacific; H.B. Fuller G3556; and Henkel 51-1057- FD. The adhesives may be used together and/or alone.

In one preferred embodiment, when a single adhesive is used, it is preferably that it be a hot-melt adhesive. In another preferred embodiment, when more than one adhesive is used, it is preferably that at least one hot-melt adhesive and at least one cold-set adhesive be utilized. The adhesives may be contained in a single layer or multiple layers and may follow the example of the substrate discussed above in relation to Figure 6 in a manner that could assume multiple different adhesive layers 5 therein Figure 6 discussed above. The individual adhesive layers may interpenetrate each other as well as the functional layer and/or web of cellulose fiber at any degree.

When two layers of cellulose fiber web are incorporated into the above-mentioned substrate of the present invention, a portion of the functional layer may intervene between the two webs at some time, which may cause a reduction in the adhesive properties of the adhesive layers thereon to adhere the webs together. Therefore, the efficiency of such converting processes may be compromised by the functionality in the functional layer present on/in the paper substrate at the time of the above-mentioned conventional converting steps. In such cases, it may be preferable to expose at least a portion of at least one layer of cellulose fiber web to the adhesive layer before and/or during and/or after adhesive layer application. Alternatively and/or in addition to such exposure, it may be desirable to increase the surface area of contact between the adhesive layer and the functional layer. Preferably, both the increase in surface area and the

exposure methodologies in combination is an embodiment of the present invention. Such portions of the paper substrate may be referred to as “treated” portions.

Means for exposing at least a portion of at least one layer of cellulose fiber web to the adhesive layer or means for increasing the surface area of contact between the adhesive layer and the functional layer may include any means for compromising at least a portion of the functional layer. Such means may include, for examples, means for penetrating, abrading, skiving, boring, breaking, busting, cracking, diffusing, drilling, eating through, encroaching, entering, goring, impaling, infiltrating, inserting, piercing, knifing, perforating, permeating, pervade, pop in, pricking, puncturing, reaming, spearing, stabbing, wearing, chafing, eroding, grating, rubbing, scraping, scratching, scuffing, denting, fragmenting, nicking, notching, paring, scratching, shaving, slicing, and splintering. Any conventional above-mentioned means commonly known to the skilled artisan, especially papermaking, is suitable, including a combination thereof. These means may be added to any conventional papermaking process and/or converting process, and/or those papermaking and/or converting processes mentioned herein, especially those processes that lead to the production of paper-based packaging systems.

An example of a converted blank for a package that contains at least one substrate of the present invention is shown as Figure 4 and may also be mentioned in United States Provisional Patent Application having USSN 60/702,879, filed July 27, 2006, which is hereby incorporated in its entirety, herein by reference. Figure 5 is a close-up view of a portion of a flap of the package blank in Figure 4. In order to fold the blank in Figure 4 into a package, it may be necessary to contact the flap in Figure 5 with another portion of the blank in a manner in which portions of the blank must

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contact each other and maintain uncompromised adhesion thereto. Accordingly, in this example, an adhesive layer may be applied thereto the substrate. Figure 6 demonstrates a first region of the flap shown in Figure 5 that corresponds to two geographies on the flap upon which the adhesion may occur. Figure 6 shows an untreated portion. Figure 7 shows a treated portion as defined above. In this specific example, the treated portion is skived.

In some instances, it is not desirable to perform any of the above mentioned means for treating the substrate, yet the presence of the functional layer could greatly reduce ability of substrates to adhere to one another. In such cases, not any conventional adhesive may be used in the adhesive layer. Preferably, the adhesive should provide an open time of from 0.5 to 5.0, more preferably 1.5 to 3.5 seconds, most preferably 1.9 to 2.5 seconds. In addition and/or in alternative, the adhesive should provide a dwell time for compression of 0.25 to 1.5 second, preferably 0.5 to 1.25 seconds, more preferably from 0.65 to 0.85 seconds. In addition and/or in alternative, the adhesive must satisfy the below mentioned initial fiber tear test (Hot melt Bonding Test attached below) which is the use of a Rock-Tenn hot melt simulator (see Examples) using settings of, 300 to 450 deg F, preferably from 350 to 380 deg F, the above-mentioned open time (preferably ~2.5 sec open time), with the above-mentioned dwell time (preferably ~0.75 sec dwell time), and with tearing force applied immediately after dwell time to simulate springback forces during conversion of packages made from the substrate of the present invention.

The Hot Melt Bonding Test provides a value of simulating the hog melt gluing process in the lab

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so as determine the effects of major variables such as substrate, adhesive, temperature, open and dwell times, and adhesive amount upon gluing. In the present application, this test was performed in the lab when two strips of paper are cut CD (cross direction) long: 2.5" x 8" and 1" x 8" specimens respectively. The adhesive is applied at the temperatures ranging from 350 to 400 degree F to the uncoated side of the 2.5" x 8" specimen with a 1.5 second of open time. The coated side of the second 1" x 8" is compressed onto this for 1.0 seconds of compression time. The samples are glued, cooled, and torn along the length of the glue bead at TAPPI Standard Conditions (73 degree F, 50% Relative Humidity).

If the initial fiber tear test mentioned above, a fiber tear test resulting in:

- a. 50-75% initial fiber tear to have a working solution would preferably require a cold-set adhesive (below this level one may not even achieve adequate bonding to hold flaps)
- b. 75 - 100% initial fiber tear to have a working solution that may or may not require a cold-set adhesive (see item #4). A cold set adhesive may be optional if this is the initial fiber tear results. However, then a test four 4 hours of curing to the substrate is begun (Four hour cured fiber tear test relates to use of Rock-Tenn hot melt simulator using settings of, 300 to 450 deg F, preferably from 350 to 380 deg F, the above-mentioned open time (preferably 2.5 sec open time), with the above-mentioned dwell time (preferably 0.75 sec dwell time), with samples stored at TAPPI standard conditions (73 F, 50% RH) under no applied load, and then torn after four hours of curing). If, after the 4 hour test, there remains a 75 - 100% initial fiber tear, then sufficient bonding occurs with the first adhesive, preferably a hot-melt adhesive, alone and the cold-set adhesive is optional. If, however, < 75% fiber tear occurs after the 4 four hour test mentioned above, then a cold set adhesive assist would be desirable in addition to the first adhesive,



preferably a hot-melt adhesive.

The present invention is explained in more detail with the aid of the following embodiment example which is not intended to limit the scope of the present invention in any manner.

## EXAMPLES

Packagings for fruits and vegetables have had problems with their inability to protect their handlers and the produce contained therein from deadly predators. Accordingly, it has been desirable to treat the packages so that the environment, in which they lie, while in transit to the consumer, in part results in their exposure to sulfur dioxide.

Sulfur dioxide is known to kill predators of produce and pests of humans. One such pest is the black widow spider. It is necessary to keep black widow spiders away or dead when in contact with the produce package and environment. Therefore, it is desirable to have a packaging material for the product that does not absorb, adsorb, and/or chemically react with the sulfur dioxide in the shipping environment. Such interactions will inevitably reduce the amount of active sulfur dioxide within the environment; thereby reducing the efficacy of the killing/controlling pests sensitive to sulfur dioxide such as black widow spiders.

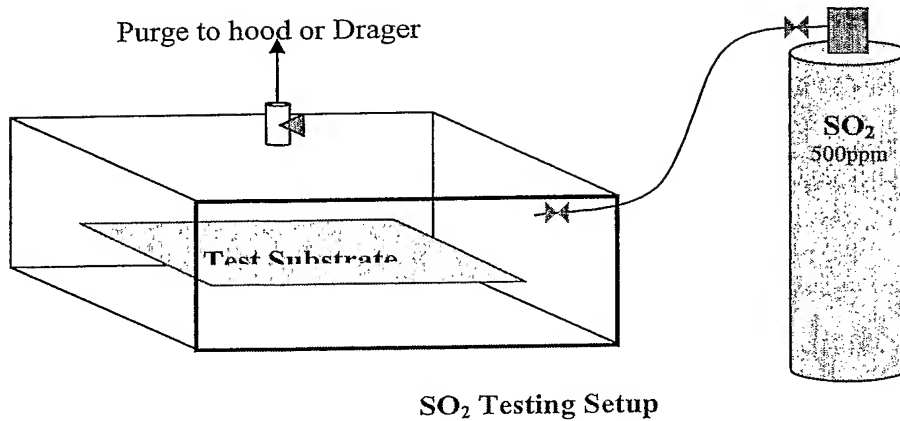
Until now, the only effective packaging material to ship such produce effectively and resist the sulfur from absorbing, adsorbing, and/or chemically reacting with such material is Styrofoam. However, Styrofoam is not environmentally friendly. Therefore, the market still demands an

environment-friendly packaging material that is capable of shipping produce at low cost and not absorb, adsorb, and/or chemically react with the sulfur dioxide in the shipping environment to the point that the active sulfur dioxide is reduced so that it is ineffective in keeping pests away and/or killing them.

As one specific non-limiting embodiment of the present invention, the inventors have surprisingly found a cellulose-based packaging material that is capable of shipping produce at low cost and not absorb, adsorb, and/or chemically react with the sulfur dioxide in the shipping environment to the point that the active sulfur dioxide is reduced so that it is ineffective in keeping pests away and/or killing them. This one non-limiting embodiment of the present invention is a paper substrate containing a functional layer that specifically increases the hold-out capacity of the substrate to sulfur dioxide. Measurement of hold-out capacity is discussed below. Preferably, the hold-out capacity is increased at least 1%, more preferably more than 5%, most preferably more than 20% as compared to substrates that do not contain this non-limiting embodiment of the functional layer. Further, the inventors have surprisingly found solutions to minimize the effect of a functional layer (e.g. sulfur dioxide holdout layer in this example) of a paper substrate on the manufacturing/converting costs/problems, while maintaining functional and structural performance of a package that incorporates the substrate therein.

The sulfur dioxide testing setup is described on the next pages, including initial attempts to physically (such as taping edges of substrates) and chemically (changing the amounts and types of chemistries contained by the functional layer of the substrates tested).

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- Plexiglas Box Dimensions: 14" x 11" x 8" = 1232 in<sup>3</sup>
- SO<sub>2</sub> is purged at 500ppm
- Once sample is in the chamber screws and electrical tape are used to seal and prevent SO<sub>2</sub> leakage.
- Glass Drager Sulfur Dioxide 20/a detection tubes are used to find residual SO<sub>2</sub> after a predetermined period of time.

**Substrate:**

- The most common substrate used in this experiment were 10" x 12" pieces of cardboard with a white liner on one side.
- 6 or 1 boards were used at a time and they could have taped or untapped edges.

**Time points taken (i.e. measurement of sulfur dioxide in ppm in the atmosphere, thus hold out).**

0 min

5 min

15 min

## Initial Screening of Physical Barriers and Chemicals For Functional Layer

Table 1: Initial Barrier Screening

<u>Conditio</u> <u>n</u>	<u>tape</u> <u>d</u>	<u>gsm</u>	<u>Chemical</u>	<u>additiv</u> <u>e</u>	<u>0</u> <u>MIN</u>	<u>5</u> <u>MIN</u>	<u>15</u> <u>MIN</u>
-			empty chamber		280	280	245
-			Styrofoam		280	250	180
-			Brown Kraft both sides		280	80	
-			white liner both sides		280	70	
35	tape d	3	Dow SA Latex 229805		280	100	
36	tape d	7	Dow SA Latex 229805		280	185	145
40	tape d	10	Dow SA Latex 229805		280	210	160
42	tape d	10	Dow SA Latex 229805 / Ethylated starch		280	180	120
41	tape d	15	Ethylated starch		280	150	80
27	tape d	3	EvCote PGLR-30		280		

11	tape d	15	EvCote PGLR-30	clay	280	220	175
37	tape d	3	V-723 Barrier Topcoat		280	60	
38	tape d	7	V-723 Barrier Topcoat		280	130	55
1		0	Control, no coating		280		
28		3	Dow SA Latex 229805		280	60	
36		7	Dow SA Latex 229805		280	100	
8		15	Dow SA Latex 229805		280	145	70
17		15	Dow SA Latex 229805	clay	280	140	60
7		15	Dow styrene acrylate 229804		280	80	
16		15	Dow styrene acrylate 229804	clay	280	130	60
24		15	Ethylated starch		280	50	
39		7	Ethylated starch		280	95	
5		15	EvCote PBWR-40		280	75	
14		15	EvCote PBWR-40	clay	280	105	
26		3	EvCote PGLR-30		280		
25		7	EvCote PGLR-30		280	100	60
2		15	EvCote PGLR-30		280	100	50
19		15	EvCote PGLR-30	talc	280	140	60
3		15	EvCote PHB-50		280	125	50

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4		15	EvCote PWRHF-40		280	120	50
13		15	EvCote PWRHF-40	clay	280	120	60
34		7	Evote PWRHF-40		280	100	55
22		15	Michem Emulsion 34935		280		
21		15	Michem Emulsion 39235		280		nd
9		15	Permax 803		280	120	50
18		15	Permax 803		280	100	50
15		15	Rhoplex P376	clay	280	140	70
20		15	Rhoplex P376	talc	280	120	
6		15	Rhoplex P376		280	120	
10		15	starch/pvoh	talc	280	100	
30		3	V-723 Barrier Topcoat		280		
38		7	V-723 Barrier Topcoat		280	80	
23		15	V-723 Barrier Topcoat		280	140	60

The above mentioned timepoint measurements are in ppm of sulfur dioxide. Therefore, the higher the number, the more sulfur dioxide measured in the atmosphere, and the more effective the functional layer-containing substrate is to sulfur dioxide holdout.

In this specific embodiment, it is preferably to have a functional layer that had sulfur dioxide holdout of any kind at 5 and/or 15 minutes respectively, preferably from 5 to 100 % holdout based upon the total amount of sulfur dioxide initially present in the atmosphere, more

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preferably from 10 to 100% holdout based upon the total amount of sulfur dioxide initially present in the atmosphere, most preferably from 50 to 100% holdout based upon the total amount of sulfur dioxide initially present in the atmosphere. The amount of holdout may be greater than 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 99% holdout based upon the total amount of sulfur dioxide initially present in the atmosphere, including any ranges and subranges therein.

### Initial Barrier Screening cont.

The results in tables 1, 2, 3 were tested under different conditions.

**Table 2: Condition 12 was tested at 3 boards instead of the standard 6 and purged for 2:45 min at the start**


<u>Conditio</u> <u>n</u>	<u>taped</u>	<u>gsm</u>	<u>Chemical</u>	<u>additive</u>	<u>0</u> <u>MIN</u>	<u>5</u> <u>MIN</u>	<u>15</u> <u>MIN</u>
12		15	EvCote PHB-50	clay	280	180	160
12	taped	15	EvCote PHB-50 TAPED	clay	280	250	220

**Table 3: Condition 31-33 tested the median board only (9"x9")**

<u>Conditio</u> <u>n</u>	<u>tape</u> <u>d</u>	<u>gsm</u>	<u>Chemical</u>	<u>0</u> <u>MI</u> <u>N</u>	<u>5</u> <u>MI</u> <u>N</u>	<u>15</u> <u>MI</u> <u>N</u>
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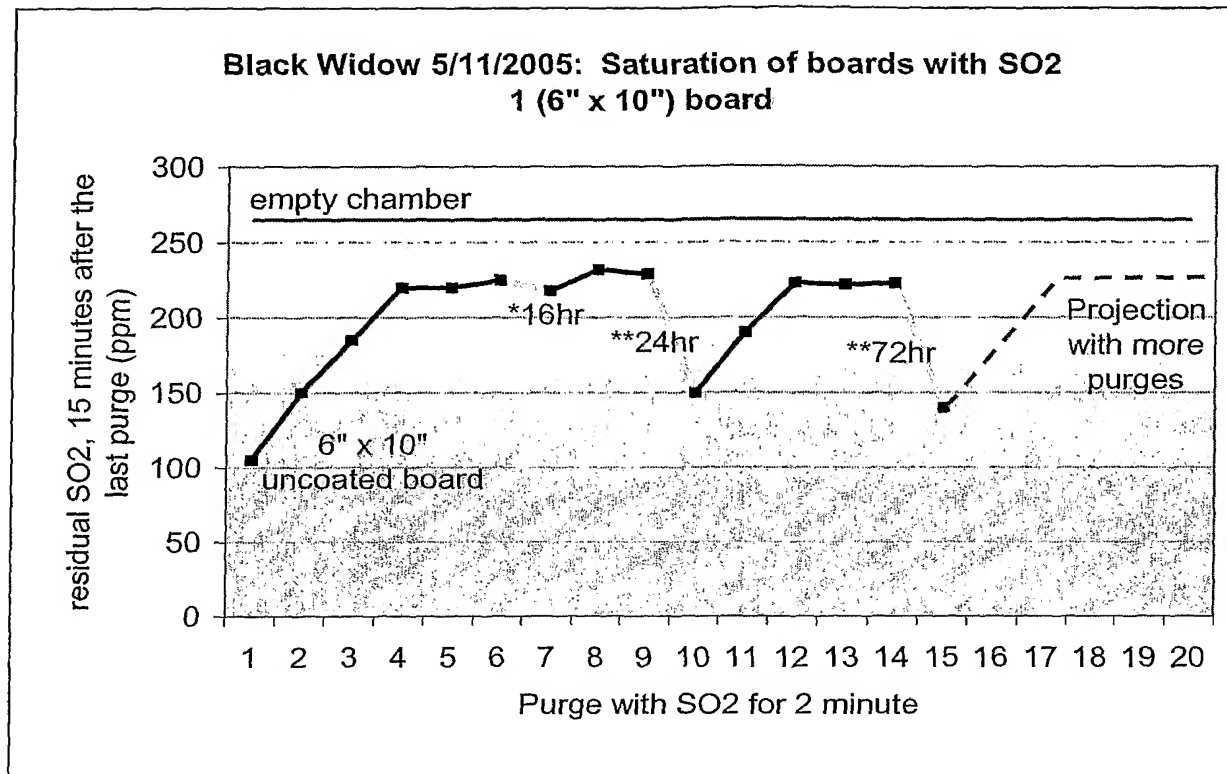
31	0	Control no coating	280	95	
32	3	Ethylated starch (boards were warped)	280	135	75
33	3	V-723 Barrier Topcoat	280	125	90

## Saturation point of SO<sub>2</sub>

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A saturation point of SO<sub>2</sub> in the board was determined by purging the boards and then waiting 15 minutes to test SO<sub>2</sub> levels. Initially six (10" x 12") boards were used with one minute purges but it was taking too long to reach a saturation level (5ppm increase per purge), so we cut the sample to one 6" x 10" board in the chamber with 2 minute purges.

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Saturation point of a 6" x 10" piece of cardboard. Usually purges were done immediately after the previous SO<sub>2</sub> measurement; those that were not are indicated.

### Testing of products currently available

- 6 (10" x 12") pieces, purge for 1 minute with SO<sub>2</sub>
- initial concentration is 260 ppm

**Table 4: Products currently available**

Material	@ 5min	@15min
Carolia C1S Cover (not corrugated – less material)	150	110
Wax board (corrugated)	200	130

### Screen pigments with improved glueability

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**Table 5: Pigment screening for glueability. One (10" x 12") board per test.**

Sample	GSM	5min	15 min
Control (no coating)	0	80	45
PEG	170	200	165
Clay (Nuclay) : Dow 229805 (1:1 ratio)	13.5	180	155
MHPC	5	180	150
GCC (Covercarb HG) : Dow 229805 (1:1 ratio)	13	180	150
Dow SA Latex 229805	13.5	180	150
Clay (Nuclay) : Dow 229805 (1:1 ratio) pH 3	13	205	150
R9320	10	160	145

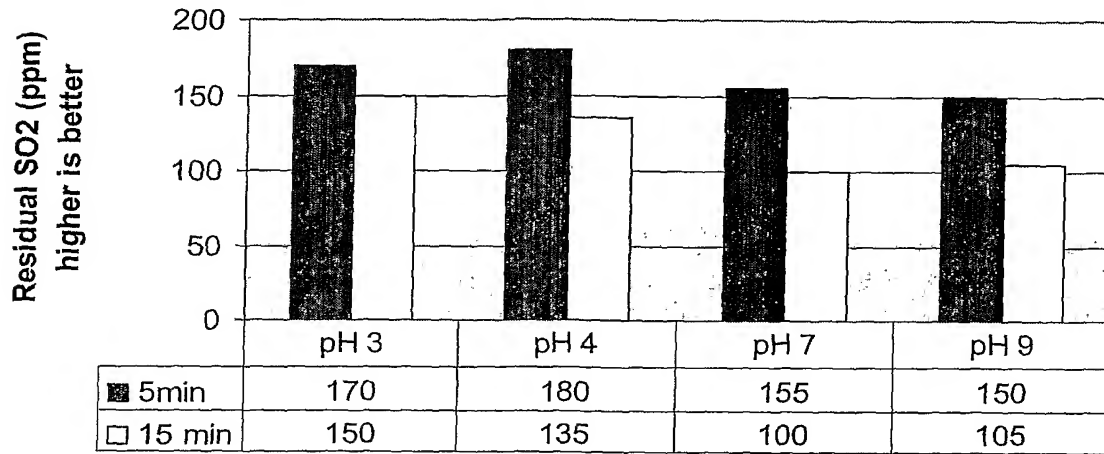
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Talc (Heliocote MT) : Dow 229805 (1:1 ratio)	13.5	185	145
PCC (Albafil) : Dow 229805 (1:1 ratio)	13.5	165	140
Clay (Nuclay) : Dow 229805 (2:1 ratio)	13.5	195	140
PVOH 523	13	175	135
GCC (Covercarb HG) : Dow 229805 (2:1 ratio)	13.5	180	130
MHPC	2.6	160	105
Clay (Nuclay) : Dow 229805 (3:1 ratio)	13.5	155	100
GCC (Covercarb HG) : Dow 229805 (3:1 ratio)	13.5	130	55
2% Lactic acid	Applied	104	50
Silica (P412) : Dow 229805 (1:1 ratio)	15	110	50
Na <sub>2</sub> SO <sub>3</sub>	6	80	

### Effect of pH on SO<sub>2</sub> barrier

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**Black Widow 5/24/2005: Effect of pH on residual SO<sub>2</sub>  
(4 handsheets)**



the effect of pH on SO<sub>2</sub> absorption.

**Test glueability: Table 6**

Samples were coated on the liner board at 13-15 gsm

- Clay (Nuclay) : Dow 229805 (1:1 ratio) **GOOD**
- Clay (Nuclay) : Dow 229805 (1:2 ratio) **GOOD**
- GCC (Covercarb HG) : Dow 229805 (1:1 ratio) **POOR**

## Boards with the Pigment:Dow formulations

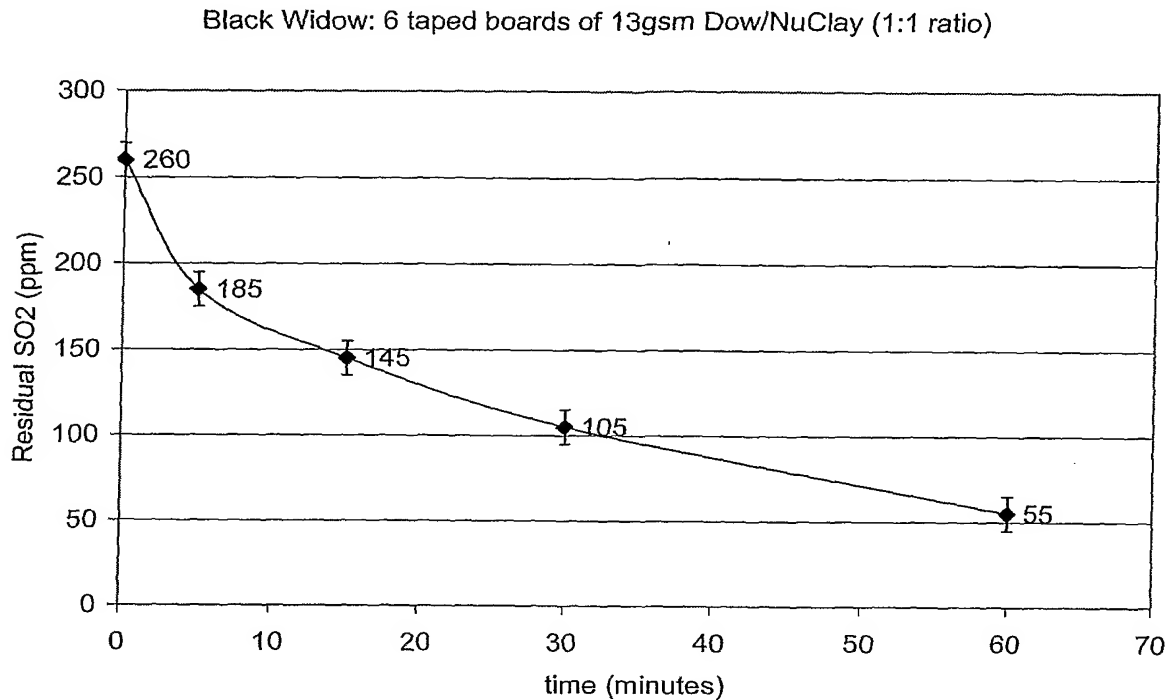


Figure 4: Residual SO<sub>2</sub> Concentration over time using 6 boards.

## Submersion of board into coating: Table 7

- Boards were cut in half and dipped into coating for 5 seconds, removed and dried. The Nuclay: Dow Latex 229805 (1:1 ratio) was used and coat wt was controlled by % solids.

Ctg	% Solids	GSM estimate	SO <sub>2</sub> after 5 min	15 min
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<b>1</b>	<b>12.5%</b>	<b>6</b>	<b>100</b>	<b>50</b>
<b>2</b>	<b>25%</b>	<b>15</b>	<b>180</b>	<b>150</b>

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**Table 8: High solids Coating; Nuclay: Dow Latex 229805 (1:1 ratio)**

- 
- Boards are coated as usual except with a 50-57% solids solution instead of the usual 20-30%. This should increase the dry time and force the coating to stay on top of the sheet instead of being absorbed in between the fibers

Coating	GSM	% solids	SO <sub>2</sub> @ 5 min	15 min
Nuclay: Dow Latex 229805 (1:1 ratio)	11	56.9	170	140
Nuclay: Dow Latex 229805 (1:1 ratio)	18	50	170	120

**Example 2:**

Apply Dow latex based and starch coatings onto liner and medium which will be used to make corrugated boxes with improved SO<sub>2</sub>/moisture barrier performance for grape packaging applications.

**Basestock**

- 69 BTWS (12,000 liner feet)
- 62ag (14,000 liner feet)
- 2 rolls of 26c (total of 50,000 feet)

**Table 9: Coating Formulation**

<i>Chemicals</i>	Coating Formulation A	Coating Formulation B



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	(Station 1 - C2S coater)	(Station 3 – C1S coater)
Dow latex 229804	100	
Cartabond TSI		1.5
NuClay	100	
Ethylex 2035 Starch		100
Defoamer	200 PPM	100 PPM
Solids	57 – 58%	15%
Target pH	5 - 7	5 - 7
Brookfield Viscosity, #2 @ 100 rpm (cps)	100 - 150	TBD

Coater Operation\*: Functional layer was applied via coater

Table 10: Coating Conditions of Linerboard substrates and/of fluting

Coating Conditions	A/Station 1 - C2S coater	B/Station 3 - C1S coater	Base Stock	Oven Temp.	Liner Feetage
Pre-run 1	C1S - side 1		62 ag	TBD	Try different rods, enough for Coat weight check
Pre-run 2	C2S		62 ag	TBD	
Pre-run 3	C1S - side 1	C1S – side 2	62 ag	TBD	
1	C1S – side 1		62 ag	TBD	4,000
2	C2S		62 ag	TBD	4,000
3	C1S - side 1	C1S – side 2	62 ag	TBD	2,000

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4	C1S – side 1		69 BTWS	TBD	4,000
5	C2S		69 BTWS	TBD	4,000
6	C1S - side 1	C1S – side 2	69 BTWS	TBD	2,000
7**	C1S - side 1		26c	TBD	14,000
8**		C1S – side 2	26c	TBD	14,000

\*Coating speed: start at 200 feet/min. Target: 400 feet/min.

**Coat weight:**

Formulation A, target: 9 lb/3 MSF (Min. 8 lbs, Max. 10 lbs) (this is 14.4 gsm)

Formulation B, target: 7 lbs/3 MSF (or as high as the machine can pick up) (this is 11.2 gsm)

**Curl control:** apply steam if necessary to obtain a flat board

**Coating width:** 76"

**Mositure level:** 4 – 6%

**Table 11: Box Construction Plan wherein the box contains three of the following substrates\***

Corrugation Conditions	1	2	3	4	5	6	7	8	9
C1S- 62 ag; coating cond. 1							+	+	+

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C2S- 62ag: coating cond. 2				+	+	+			
C1S/C1S- 62ag: coating cond. 3	+	+	+						
C1S- 26c coating cond. 7			+	+					+
C1S- 26c coating cond. 8	+				+			+	
Uncoated 26c		+				+	+		
C1S- 69 BTWS coating cond. 4							+	+	+
C2S- 69 BTWS coating cond. 5				+	+	+			
C1S/C1S- 69 BTWS coating cond. 6	+	+	+						

one control was run using the two uncoated liner and medium before or after the trial.

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**Example 3**

The same as the proposed Box Construction Plan in Example 2, except a 74 lb paper substrate was put in to replace the 69 lb substrate. Condition 3 mentioned below was then converted to a package and/or box so as to be Box #3. Therefore, unless specifically mentioned otherwise below, the DuraCool box or International Paper box # 3 corresponds to a box that was made from Condition #3 mentioned below.

The above-mentioned box blanks were successfully converted to trays at the using Boix MP-S equipment using several hot melt adhesives with a cold glue assist. There were three major gluing scenarios, all of which produced well-bonded DEFOR Black Widow grape trays:

1. The highest degree of initial fiber tear was obtained using the National 34-6601 hot melt. This adhesive was difficult to apply due to its high viscosity even at a gun temperature of 380 degree F. Timing adjustments were required on the Boix MP-S to accommodate the delays in getting it to feed through the Nordson nozzles.
2. The HB Fuller Advantra HL9254 and the reformulated Chief 235 Plus adhesive also produced well bonded trays; however, these rely heavily on the cold set adhesive (Henkel 51-1057-FD) to achieve fiber tear. The trays leaving the Boix are well-bonded but do not exhibit fiber tear until the cold set glue is cured. These hot melts were easier to apply at a gun temperature of 350 degree F.
3. An additional condition was conceived during the trial and has promise for being the lowest cost solution: skiving of the glue flaps of the tray, which exposes uncoated linerboard surface, and use of the standard Henkel hot melt adhesive (Henkel 80-7883) with cold glue assist. The trays

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formed using this method were well bonded and achieved a high degree of integrity and fiber tear.

### INITIAL TRIAL

The initial hot melt adhesives recommended by Henkel, Chief Adhesives and National Starch did not set quick enough through the Boix MP-S equipment to hold the flaps of the tray together and/or had poor bonding and fiber tear. The adhesives trialed in the first trial are listed below.

Table 12

### INITIAL CONVERTING RESULTS

Hot Melt Adhesive	Performance Notes
Henkel 80-8795	High initial tack to latex coated liner, but does not set quick enough to hold flaps of tray together. A high viscosity product that is difficult to feed at 360 F. A number of temperatures, pressures were trialed with little success. This adhesive is typically used to bond polypropylene corrugated board.
Chief 235 HP	Quickest set time but inadequate fiber tear. Worked better than the Chief adhesive used for poultry boxes (261 HP).
National 34-246A	Less successful than the Henkel 80-8795. Could not obtain adhesion at the short compression time. Trialed a variety of glue temperatures with little success.

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The major issue which the first trial uncovered were the following:

1. The Boix MP-S presents a challenge in that it operates with a long open time of 1.9 to 2.5 seconds (start of glue to end of glue bead application) followed by a compression dwell time of only 0.75 seconds (time in which flaps held together by equipment) at typical operating speeds. The hot melt glue must stay molten during this long open time and then set up and solidify quickly during the subsequent compression time. Running at slower speed on the Boix would increase the compression time slightly, but reduce converting efficiency.

#### LABORATORY ADHESIVE EVALUATION IN LIGHT OF THE ABOVE

##### Lab Hot Melt Adhesive Tests

To better simulate the Boix equipment, the hot melt gluing test using the Rock-Tenn simulator was modified so that a springback force was applied manually following the compression cycle (SEE THE ATTACHED FORHTE ROCK-TENN LAB TESTER INFORMATION AND METHODOLOGY). The most recent latex coated liner was used as the substrate with an open time of 3 seconds and compression time of 0.75 seconds in the following tests:

Table 13

#### LABORATORY COMPARISON OF HOT MELT CANDIDATES

Adhesive	Degree of immediate fiber tear	Degree of fiber tear after 4 hours	Application Temp & Viscosity	Anticipated price per pound
Chief 235 Plus	Good (>75%)	None (clean peel)	350 F/ low visc	\$1.50

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HB Fuller HL9254	Excellent (~100%)	None (clean peel)	350 F/ low visc	\$1.50
Henkel TB9-15-5	None (still tacky)	Excellent (~100%)	350 F/ med visc	TBD
National 34-6601	Excellent (~100%)	Good (>75%)	380 F/ high visc	\$3.50
National 34-379A	Good (>75%)	Excellent (~100%)	380 F/ high visc	\$3.50

### Lab Hot Melt Results

- All of the hot melts with the exception of Henkel sets quickly. All develop significant fiber tear and tack initially (tested within 10 seconds after compression) which may be sufficient to hold the flaps of the tray together.
- The hot melt which gives the poorest initial results is the Henkel TB9-15-5. This remained stringy and rubbery after the compression and springback. However, once it set it gave a very high bonding force with complete fiber tear. The problem is that it may not set fast enough through the Boix equipment.
- Given the fact that we will have a cold-set adhesive assist on this tray design, the Chief 235 Plus and the HB Fuller HL 9254 may do the job of keeping the flaps of the tray together long enough for the resin adhesive to penetrate and to develop fiber tear.
- The two products by National Starch (34-6601 and 34-379A) are polyamide hot melts which have the best performance. However, they are so viscous that there may be problems delivering them through the Nordson equipment on the Boix machine and achieving a uniform length and width glue bead. Of the two, the 34-6601 is less viscous

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and still has very good performance. Note that these had to be applied at 380 degree F rather than 350 degree F to get them to feed through our lab Nordson setup.

### **Lab Cold-Set Adhesive Tests**

The goal of the cold set glue tests was to determine the degree of fiber tear achieved with the latex coated liner and the time to achieve complete fiber tear. The resin (polyvinyl acetate formulation) adhesive was applied with a 0.015-inch Bird bar to the felt side of the latex coated liner and a second specimen of the treated liner was placed felt side down onto the first strip and compressed at 0.3 psi for the duration of the test. The time was varied in intervals from 5 to 28 minutes and the degree of fiber tear was noted for each test. The table below shows the minimum time at which 100% fiber tear was noted for each adhesive:

**Table 14**

### **LABORATORY COMPARISON OF COLD-SET ADHESIVES FOR BLACK WIDOW**

<b>Cold-Set Adhesive</b>	<b>Minimum Time to Develop 100% Fiber Tear (minutes)</b>
Forbo/Swifts *	8
Pacific *	12
H.B. Fuller G3556	16
Henkel 51-1057- FD *	26



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\* The HB Fuller G3556 adhesive is a high performance commercial adhesive used on folding carton grades used for reference.

With untreated linerboard, the time to develop 100% fiber tear is in the range of 10 to 30 seconds. Therefore, the latex coating significantly retards the rate of absorption of the water-based adhesives, but still achieves complete fiber tear.

Based upon the above, the cold-set glue adhesive is recommended at this time when used along with the hot melt glue even on the boxes to provide their high temperature resistance. As the grapes boxes are stored and packaged in temperatures sometimes exceeding 110 degree F, hot melt glue alone would soften leading to pop-opens unless there was cold-set glue to provide a strong bond that can resist temperature extremes.

Although the comparison of times to achieve complete fiber tear is useful to understand the dynamics of absorption, the recommendation must also consider the ability of each of the cold-set adhesives to create a thick enough film to bridge the gap between the two surfaces of the coated linerboard in the glue flap region. As it turns out, the product with the slowest absorption rate creates the thickest film which persists long enough to effectively bond the two surfaces of the board.

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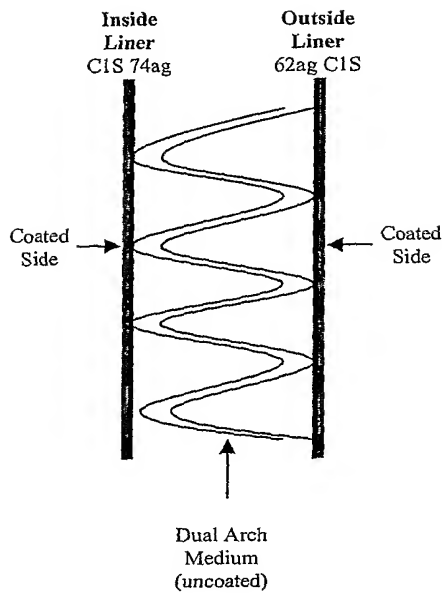
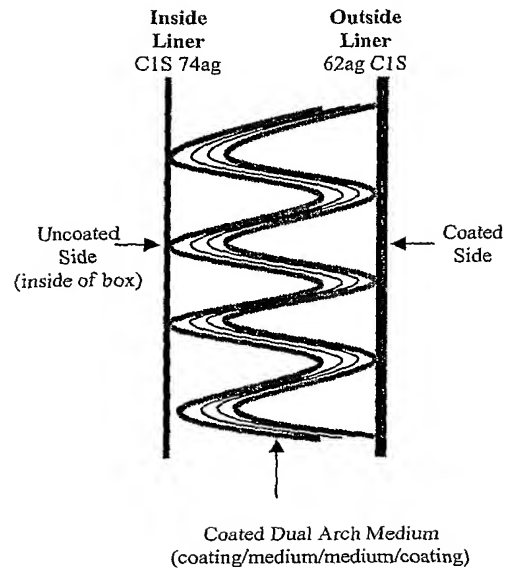
**SECOND CONVERTING TRIAL**

The goal of the second converting trial was to evaluate the various hot melt adhesives and to produce enough trays for the long term storage

There were two board conditions that were trialed (condition numbers relate to prior coating and corrugating trials):

- **Condition 3** in Table 11 above (i.e. C1S latex 74 ag / uncoated 26c media/ uncoated 26c media / 62 ag C1S latex)
- **Condition 5** in Table 11 above (i.e. uncoated 74 ag / latex coated 26c media/ latex coated 26c media/ 62 ag C1S latex)

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**Condition 3****Condition 5**

Condition 3 represents the minimum coating cost scenario in which the single-face (74 ag) and the doubleback (62 ag) liner were coated on their outer surfaces (non-flute contacting side) and the dual arch medium (26c/26c) was uncoated.

Condition 5 was a condition that was designed to be easier to glue on the Boix equipment as it had the latex on the medium and only the doubleback (62 ag) sides. The plan was to convert Condition 3 using the newer hot melt adhesives and to convert Condition 5 using the standard Henkel adhesive for comparison. As it turned out, even the Condition 5 trays had one glue flap that contained a latex coating on the DB liner side, so that it also required a higher performance hot melt. The standard hot melt adhesive does not bond to the latex coated portion of the glue

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flap, therefore this is not a viable low cost commercial solution.

The hot melt adhesive trials on the Boix MP-S equipment are listed below. It is important to note that the tray flaps held together through the Boix equipment even at the highest operating speed (24 boxes per minute (bpm)).

Table 15

**TRIAL CONDITIONS RUN ON BOIX MP-S**

<b>Condition</b>	<b>Hot Melt</b>	<b>Speed (boxes/min)</b>	<b>Tank Press (psig)</b>	<b>Tank Temp (F)</b>	<b>Hose Temp (F)</b>	<b>Gun Temp (F)</b>	<b>Cold Glue used?</b>
3A	HB Fuller HL9254	16	50	365	350	350	No
3B	HB Fuller HL9254	24	50	365	350	350	No *
3C	HB Fuller HL9254	24	50	365	350	350	Yes
3D	Chief 235 Plus	24	50	365	350	350	Yes
3E	Chief 235 Plus	24	50	365	350	350	Yes

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3F	Chief 235 Plus	16	50	365	350	350	No
3G	National 34-6601	16	75	390	380	380	No
3H	National 34-6601	24	75	390	380	380	No
3I	National 34-6601	24	75	390	380	380	Yes

\* Note: A very small amount of cold set adhesive trickled onto a portion of Condition 3B, but this was much less than that applied on Conditions 3C, 3D, 3E and 3I.

### **Overnight Stacking**

Stacks of trays 25 high with an additional 40 lbs. of weight at the top of the stack of each of the nine conditions were placed outside the plant in direct sunlight to determine whether any of the flaps would open. Conditions #3A, B and C were outside for approximately 3.5 hours; Conditions #3D, E and F were outside for approximately 3 hours; Conditions #3G, H and I were outside for approximately 1.5 hours in direct sunlight and approximately 90 F ambient temperature. Each stack was then placed inside the plant at the conclusion of the day and was examined the next morning (September 7). All stacks of trays maintained their structural integrity on this overnight stacking test, with the exception of 2 boxes out of 25 that had one flap popping open made with the Chief 235 Plus hot melt and with no cold-set adhesive.

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**Examination of Glue Flaps**

Also, boxes of each condition number were torn open and the subjective force to open the flaps was noted. There were three key results:

- Every tray made using a combination of hot melt adhesive, regardless of type, and the cold set adhesive exhibited excellent fiber tear and a high force to rip open the glue flaps.
- The trays made with the HB Fuller HL9254 and Chief 235 Plus hot melts and with no cold-set adhesive failed at significantly lower force than those made with cold set adhesive, and they did not exhibit fiber tear.
- The trays made with the National 34-6601 polyamide hot melt and with no applied cold set also achieved significant fiber tear and had flaps failing at a high force.

**Impact of Skiving of Glue Flaps**

A condition in which the outer surfaces of the glue flaps of the blanks were roughened or perforated to determine whether the standard hot melt adhesive used on uncoated boxes (Henkel 80-7883) could successfully bond a latex coated box (Condition 3). Using a knife, the glue flaps of several trays were perforated to simulate a skiving operation that may also be used on

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folding cartons as a cold glue assist methodology. These samples were produced and demonstrated that good fiber tear could be produced even using a less aggressive hot melt adhesive.

**Sulfur Dioxide holdout of converted boxes.**

Sulfur dioxide fumigation is used by the California table grape industry for control of insects and decay in packed table grapes. The treatment for decay control is designed to achieve a minimum dose of 100 CT (concentration in ppm x time in hours), achieved by either a 30-minute treatment or a total utilization treatment. The treatment for black widow spider control is a 30-minute fumigation with 6% CO<sub>2</sub> and 1% SO<sub>2</sub>. While there is no official requirement for monitoring CTs during the black widow spider treatment, laboratory studies suggest that a CT of approximately 3,000 to 3,300 ppm·hrs is required for high spider mortality.

The type of packaging materials used can influence the concentrations of sulfur dioxide in the fumigation room during treatment due to the potential for packaging materials to absorb sulfur dioxide. Cardboard packaging material generally has a high rate of sulfur dioxide absorbance. In fact, the cardboard box is no longer approved for use in the black widow spider protocol for this reason.

**Example 4: Comparison of Various Box Types**

Initial tests included two experimental boxes, #1 and #3. For each test, two boxes of the same type were packed with 18 pounds of cold table grapes, held at 20 degree C overnight to equilibrate to that temperature, and fumigated the following day. The two boxes (25.4 liters, 0.90

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ft<sup>3</sup> each) were loaded into a sealed 165 liter chamber and the final load volume was 30.8%. The boxes were fumigated with 1% sulfur dioxide (1,900 ml 100% SO<sub>2</sub> injected) for 30 minutes at 20 degree C. The sulfur dioxide levels in the chamber were monitored at the start and every 5 minutes thereafter using a rapid gas analyzer. A 10ml sample was drawn through a rubber septum mounted on the fumigation chamber with a syringe and injected into the analyzer. The sulfur dioxide concentrations over time (CT) were calculated for each test. The results from these tests indicated that the Styrofoam boxes had the highest CT, followed by condition #3, then condition #1 and finally the regular cardboard box.

Table 16. Initial tests comparing experimental box samples with Styrofoam and cardboard grape boxes for absorbance of sulfur dioxide and final CT value following a simulated black widow spider fumigation (which requires sulfur dioxide in the atmosphere).

Box Type	Untreated Cardboard	Styrofoam	Condition #1	Condition #3
CT (ppm·hours)	1,512	4,994	2,584	2,716

In these initial tests, grapes had been placed in the boxes immediately upon removal from the cold room and allowed to warm in the box. This likely resulted in condensation within the bags which may have reduced the final CT values for all the tests. However, it was clear that box #3 had the best performance of the cardboard boxes and therefore subsequent tests focused on box



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#3. It should be reiterated that box #3 was constructed and converted from liner and medium condition #3 of Table 11 and described in more detail at page 50 above. We wondered if the amount of time the grapes were in the box after harvest would influence moisture absorbance by the box and subsequent absorbance of sulfur dioxide. In this next test, we fully warmed and dried the grapes before placing them into the cardboard boxes. The grapes were held in different sets of boxes for 2, 4, 8 and 12 hours prior to 1% sulfur dioxide fumigation as described above. There were two separate boxes for each time point.

Table 17. Effect of time the grapes were held in the boxes prior to sulfur dioxide fumigation on change in box weight and sulfur dioxide absorbance.

Hours Delay with Grapes	Weight increase of Box (%)	CT (ppm*hours)
2	0.79	2948
4	1.06	3400
8	1.40	2950
12	1.56	2698

The boxes absorbed additional weight over time, but more of the weight gain occurred in the first few hours and slowed thereafter. There was not much effect on sulfur dioxide absorbance of storing the grapes up to 8 hours in the box, but perhaps a slight decrease in CT at 12 hours. The results indicate that the final CT using box type #3 and a load factor near 30.8% would be close to 3,000 CTs and should provide for high black widow spider mortality.

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**Effect of Cold Storage**

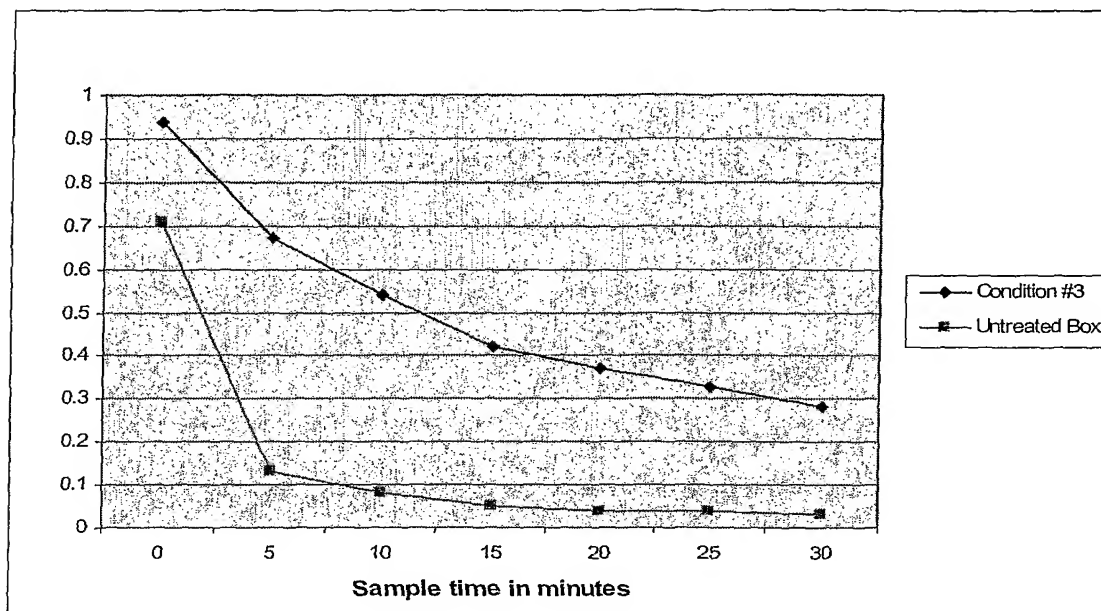
The final test involved storing a regular untreated cardboard grape box and experimental box #3 with grapes at 0 degree C for two weeks prior to sulfur dioxide fumigation at 0C. The boxes were weighed before and after cold storage to determine the amount of moisture gain during this time. Following storage, two boxes of each type were fumigated with 1% sulfur dioxide as described above and the CT values determined.

Table 18. CT values following fumigation of regular cardboard grape boxes and experimental box #3 with 1% sulfur dioxide for 30-minutes at 0 degree C following two weeks of cold storage with grapes at 0 degree C.

Box Type	CT Value	% Box Weight Gain
Regular Carboard Grape Box	581	10.12
Experimental Box #3	2,421	7.95

There was a clear difference between the CT values for the two types of boxes fumigated following two weeks of cold storage, with a four-fold higher CT value with the Experimental Box #3. The regular cardboard box absorbed more water than experimental box #3. However, the weight gain was also substantial for the experimental box, but this did not seem to greatly affect the CT value achieved during sulfur dioxide fumigation. The pattern of decline in sulfur dioxide concentration between the two box types during fumigation after cold storage is shown below.

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This graph represents the percent of sulfur dioxide in the fumigation chamber during a 30-minute fumigation with 1% sulfur dioxide. In each fumigation, two boxes of the same type, untreated cardboard boxes or experimental boxes #3 were placed in the cold room for two weeks with grapes prior to loading into the fumigation chamber at a load factor of 30.8%. The final CTs are given in Table 18 above.

## Conclusions

Our results demonstrate that the experimental boxes absorbed less sulfur dioxide during a simulated black widow spider fumigation protocol than the standard cardboard grape box. The best performance was for box #3 which achieved an 80% higher CT value than the standard cardboard box under the test conditions employed. The CTs following fumigation in box #3 were approximately 3,000. Accordingly, the present invention relates to a paper substrate that is

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capable of making a box that has a CT of more than 2000, preferably more than 2500, more preferably more than 3000. These substrate is capable of being incorporated into a box that has a CT of at least 2000, 2100, 2200, 2300, 2400, 2500, 2600, 2700, 2800, 2900, 3000, 3100, 3200, 3300, 3400, 3500, 3600, 3700, 3800, 3900, and 4000, including any and all ranges and subranges therein. Previous results from laboratory tests suggest these CT would provide for greater than 90% black widow spider mortality. In comparison, the regular cardboard grape box gave a CT of 1,500 which would provide for about 50% black widow spider mortality. Following cold storage for two weeks, both box types weighed more (presumably they absorbed moisture from the air and fruit), but the experimental box showed a smaller increase in weight and achieved a four-fold higher CT than the regular cardboard grape box. The CT achieved with box #3 (2421 ppm·hours) should provide for approximately 80% spider mortality while the CT achieved with the regular cardboard box would provide for less than 30% mortality.

The experimental box #3 developed by International Paper has been demonstrated to absorb considerably less sulfur dioxide than the regular cardboard table grape box and is worthy of further consideration as an improved packing material for the table grape industry. The reduction in sulfur dioxide absorbance would likely be beneficial for decay control and black widow spider control.

**Example 5: More Tests**

To find a suitable replacement for Styrofoam boxes used for long term storage of table grapes, several different coated boxes were developed and their performance during the sulfur dioxide fumigation was tested in our laboratory. The box of the present invention containing the substrate

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of the present invention showed the best performance. The absorption of sulfur dioxide was significantly reduced compared to the uncoated box. Its performance was also superior compared to the competitors' boxes.

### **Method of Testing**

The testing was performed in an airtight chamber with air and sulfur dioxide mixture (0.7% by weight). An empty box was placed in a testing chamber and fumigated with the gas mixture until the atmosphere in the chamber was completely exchanged. After the fumigation, the concentration of the SO<sub>2</sub> was measured periodically using Drager tubes.

### Results

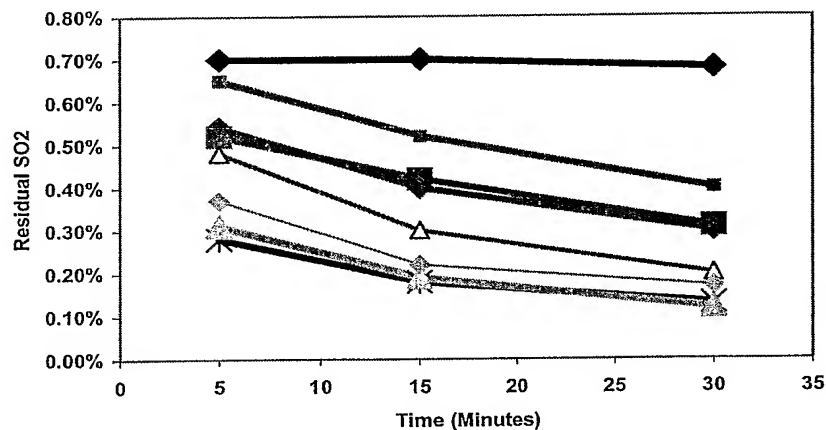
The graph below compares results of the measurements of different boxes. In order to confirm that the chamber was sealed, the empty chamber was fumigated with the gas mixture and the concentration of sulfur dioxide was measured at 15 and 30 minutes. The SO<sub>2</sub> concentration remained constant within the experimental error (see the blue line on the graph below).

The rest of the lines on the graph show sorption of sulfur dioxide by different types of boxes. The box with a better performance will have a flatter line, showing smaller change in the sulfur dioxide concentration. The Styrofoam box showed the least sorption of SO<sub>2</sub> as expected. The uncoated box caused a dramatic decrease in the sulfur dioxide concentration (orange line on the graph), which dropped more than half after only 5 minutes. The GP box (blue line) performed in a way similar to the uncoated box. The Weyerhaeuser box (green line) showed smaller sorption of sulfur dioxide, and the Maxco box performed better compared to the other two competitors'

boxes.

We tested two IP DuraCool boxes (red lines). One of them was printed, the other unprinted. The overlap of the two red lines indicates good reproducibility of the data. The performance of the box according to the present invention made from the substrate of the present invention was superior to all of the tested competitors' boxes and showed significant improvement in performance when compared with the uncoated box.

**Results of SO<sub>2</sub> Sorption Test**

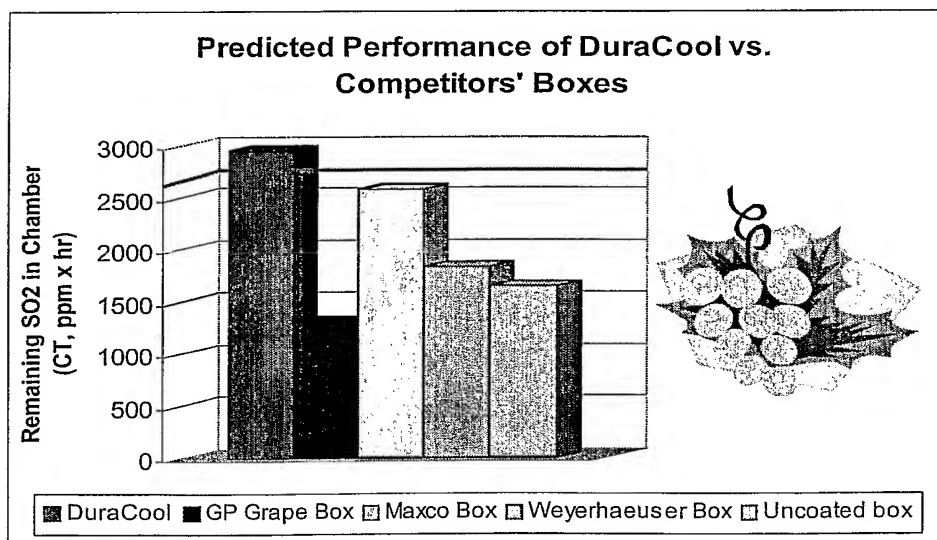


◆ Empty chamber	◆ Styrofoam	✱ GP Grape Box	◆ DuraCool printed
◆ DuraCool	◆ Uncoated	△ Maxco Box	◆ Weyerhaeuser Box

The inventive boxes were also tested in the laboratory of the Department of Plant Sciences at the University of California Davis. The testing was performed on boxes packed with grapes, using

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the chamber with load similar to that used by grape growers. The amount of sulfur dioxide introduced into the chamber was equivalent to 1% by weight. These testing conditions simulated closely the grape fumigation process prior to storage. We were not able to test the competitors' boxes the same way due to logistics, however by correlating the inventive box data (i.e. Duracool) obtained in our laboratory with the results from UC Davis, we were able to make predictions of performance of the competitors' boxes under the same conditions. The graph below illustrates the calculated predicted results. The performance of the boxes is expressed in the amount of sulfur dioxide remaining in the chamber during the treatment in units called CT (ppm x hr). The actual tested CT value for the DuraCool box was close to 3000, while the Maxco box (which was the best performing competitors' box) had the predicted CT value of 2570. Based on the results of general testing, a box having a CT of approximately 2700 or higher will provide greater than 90% black widow mortality.



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Numerous modifications and variations on the present invention are possible in light of the above teachings. It is, therefore, to be understood that within the scope of the accompanying claims, the invention may be practiced otherwise than as specifically described herein.

As used throughout, ranges are used as a short hand for describing each and every value that is within the range, including all subranges therein.

All of the references, as well as their cited references, cited herein are hereby incorporated by reference with respect to relative portions related to the subject matter of the present invention and all of its embodiments



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## WHAT IS CLAIMED IS:

- 1) A paper or paperboard substrate, comprising  
a web of cellulose fibers and a functional layer, wherein when the substrate is incorporated into a box, the box has a 100 CT (sulfur dioxide concentration in ppm x time in hours) achieved by either a 30-minute treatment or a total utilization treatment of sulfur dioxide.
- 2) The paper or paperboard substrate according to Claim 1, wherein the functional layer comprises at least one film forming compound and optionally starch.
- 3) The paper or paperboard substrate according to Claim 1, wherein the functional layer comprises optionally starch and at least one film forming compound selected from the group consisting of latex and styrene acrylate.
- 4) The paper or paperboard substrate according to Claim 1, wherein the functional layer comprises at least one film forming compound having a Tg that is not greater than 350°C.
- 5) The paper or paperboard substrate according to Claim 1, wherein the functional layer is present in the substrate at a coat weight that ranges from 5 to 15 gsm.
- 6) The paper or paperboard substrate according to Claim 1, wherein the functional layer further comprises at least one member selected from the group consisting of a crosslinker, a clay, a pigment, an anti-blocking agent, and a defoamer.
- 7) The paper or paperboard substrate according to Claim 1, wherein the functional layer and the web of cellulosic fibers have a layer of interpenetration.
- 8) The paper or paperboard substrate according to Claim 1, wherein the functional layer and the web of cellulosic fibers have a layer of interpenetration and the interpenetration layer is less than 25% of the entire cross section of the substrate.

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- 9) The paper or paperboard substrate according to Claim 1, wherein the functional layer and the web of cellulosic fibers have a layer of interpenetration and the interpenetration layer is greater than 25% of the entire cross section of the substrate.
- 10) The paper or paperboard substrate according to Claim 1, wherein the functional layer and the web of cellulosic fibers have a layer of interpenetration and the interpenetration layer 100% of the entire cross section of the substrate.
- 11) The paper or paperboard substrate according to Claim 1, wherein the functional layer and the web of cellulosic fibers have a layer of interpenetration and the interpenetration layer is greater than 100% of the entire cross section of the substrate and the functional layer is evenly dispersed throughout the web.
- 12) The paper or paperboard substrate according to Claim 1, wherein the substrate has a Cobb Value of less than 35 g/m<sup>2</sup> as determined by the Cobb Sizing Test, according to ASTM D-3285 (TAPPI T-441).
- 13) The paper or paperboard substrate according to Claim 1, wherein the substrate has an increase in sulfur dioxide holdout that is at least 5% greater than that of a substrate not containing the web of cellulose fibers and the functional layer.
- 14) The paper or paperboard substrate according to Claim 1, further comprising an adhesive layer.
- 15) The paper or paperboard substrate according to Claim 14, wherein the functional layer lies between the adhesive layer and the web.
- 16) The paper or paperboard substrate according to Claim 14, wherein the functional layer lies at least on a surface of the web and between the adhesive layer and the

web.

- 17) The paper or paperboard substrate according to Claim 16, wherein the functional layer and the web further create an interpenetration layer.
- 18) The paper or paperboard substrate according to Claim 14, wherein a portion of the functional layer lies at least on a surface of the web and between the adhesive layer and the web.
- 19) The paper or paperboard substrate according to Claim 14, wherein a portion of the functional layer lies at least on a surface of the web and between the adhesive layer and the web; and a surface of the web is also in contact with a portion of the adhesive layer.
- 20) The paper or paperboard substrate according to Claim 19, wherein a portion of the adhesive layer penetrates through a portion of the surface of the web.
- 21) A corrugated board, comprising the paper or paperboard substrate according to Claim 1.
- 22) A package, carton, or box, comprising the corrugated board according to Claim 21.
- 23) The package according to Claim 22, having a sulfur dioxide CT that is at least 2500.
- 24) The package according to Claim 22, having a sulfur dioxide CT that is at least 2700.
- 25) The package according to Claim 22, having a sulfur dioxide CT that is at least 3000.

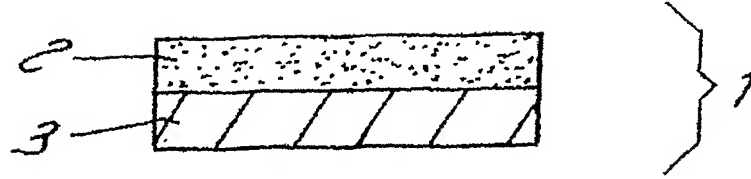


FIG. 1

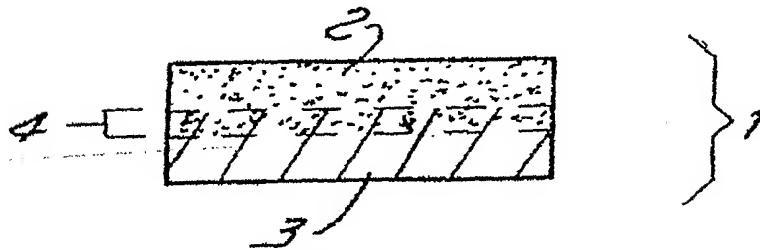


FIG. 2

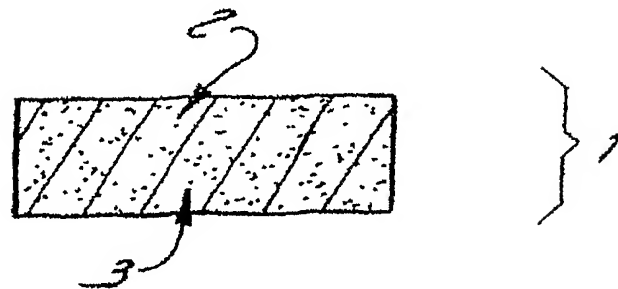
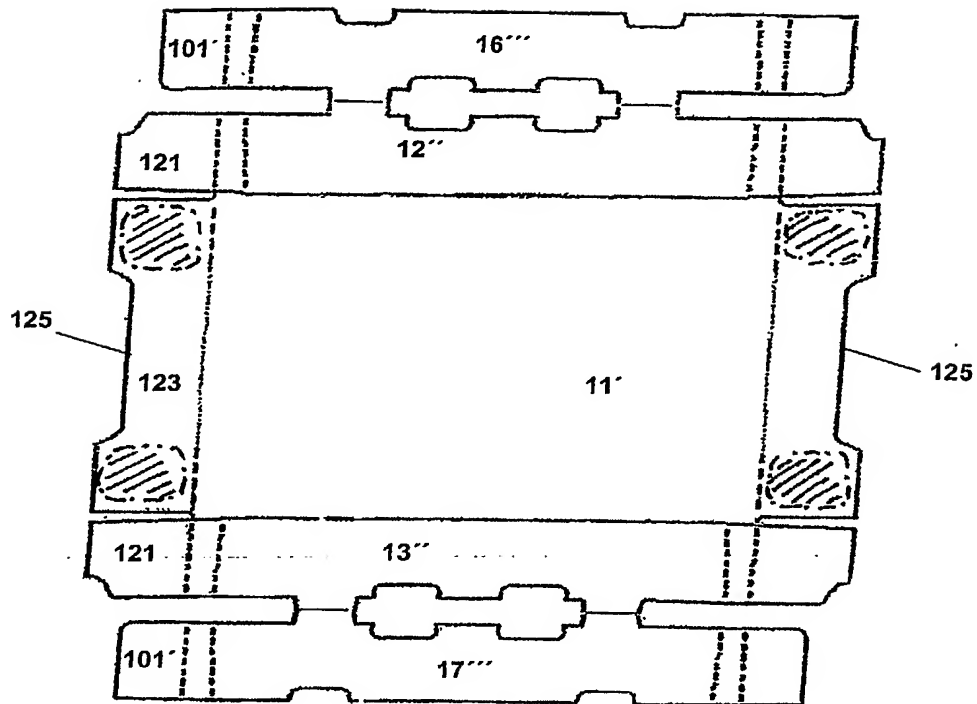
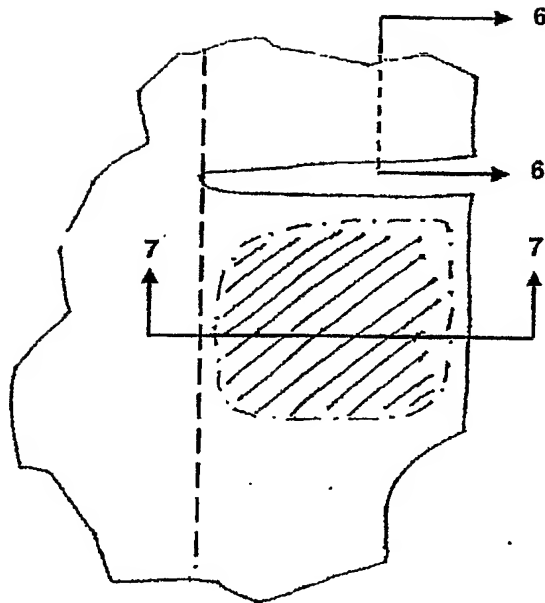


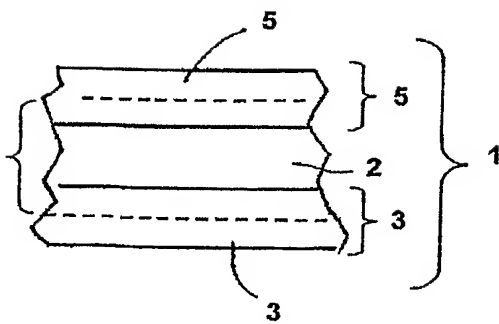
FIG. 3



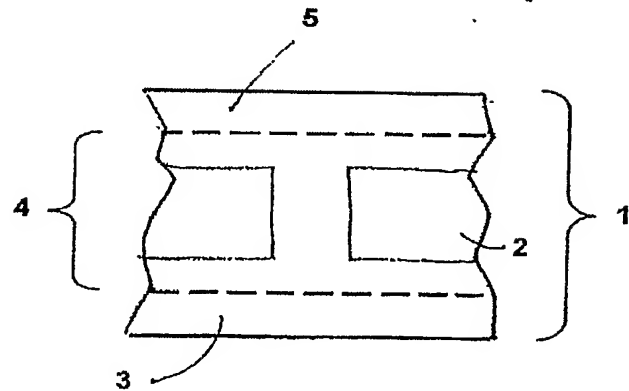
**FIG. 4**



**FIG. 5**



**FIG. 6**



**FIG. 7**

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2006/026716

## A. CLASSIFICATION OF SUBJECT MATTER

INV. D21H19/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/221976 A1 (WILLIAMS RICHARD [US] ET AL) 11 November 2004 (2004-11-11) examples	1-25
X	US 2004/005341 A1 (DIXIT AJIT S [US] ET AL) 8 January 2004 (2004-01-08) abstract	1-25



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&amp;" document member of the same patent family

Date of the actual completion of the international search

14 November 2006

Date of mailing of the international search report

30/11/2006

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Naeslund, Per

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2006/026716

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004221976	A1	11-11-2004	
		AU 2004236484 A1	18-11-2004
		BR PI0410293 A	16-05-2006
		CA 2524999 A1	18-11-2004
		CN 1802469 A	12-07-2006
		EP 1620603 A1	01-02-2006
		WO 2004099499 A1	18-11-2004
		MX PA05011818 A	17-02-2006
US 2004005341	A1	08-01-2004	NONE



**PUB-NO:** WO2007008786A1  
**DOCUMENT-IDENTIFIER:** WO 2007008786 A1  
**TITLE:** A PAPER SUBSTRATE  
CONTAINING A  
FUNCTIONAL LAYER  
AND METHODS OF  
MAKING AND USING THE  
SAME  
**PUBN-DATE:** January 18, 2007

**INVENTOR-INFORMATION:**

<b>NAME</b>	<b>COUNTRY</b>
RUDOLPH, RICHARD F	US
HONG, YAOLIANG	US
MILLER, DEREK L	US
HUANG, YAN C	US
YANG, SEN	US
SONG, JAY C	US
LIGUZINSKI, BENJAMIN THOMAS	US
BUCHER, EWA GERTRUDA	US
TAN, ZHENG	US
KULKARNI, SANDEEP	US

SHIH, KEITH S

US

**ASSIGNEE-INFORMATION:****NAME****COUNTRY**

INT PAPER CO

US

RUDOLPH RICHARD F

US

HONG YAOLIANG

US

MILLER DEREK L

US

HUANG YAN C

US

YANG SEN

US

SONG JAY C

US

LIGUZINSKI BENJAMIN THOMAS

US

BUCHER EWA GERTRUDA

US

TAN ZHENG

US

KULKARNI SANDEEP

US

SHIH KEITH S

US

**APPL-NO:** US2006026716**APPL-DATE:** July 11, 2006**PRIORITY-DATA:** US69827405P (July 11, 2005) ,  
US73402105P (November 4,  
2005)

**INT-CL (IPC):** D21H019/00

**EUR-CL (EPC):** D21H019/00

**ABSTRACT:**

CHG DATE=20070126 STATUS=O>The invention relates to the papermaking art and, in particular, to the manufacture of paper or paperboard substrates, paper-containing articles such as multilayered paper or paperboard or corrugated-based packaging having a functional layer, as well as methods of making and using the same.